



Attorney Docket No. 1022702-000319

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Olivier Larcher et al.) Group Art Unit: 1793
Application No.: 10/589,209) Examiner: John A. Hevey
Filed: May 14, 2007) Appeal No.: _____
For: COMPOSITION BASED ON)
ZIRCONIUM OXIDES,)
PRASEODYMIUM, LANTHANUM OR)
NEODYMIUM, METHOD FOR THE)
PREPARATION AND USE THEREOF)
IN A CATALYTIC SYSTEM)

APPEAL BRIEF

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This appeal is from the decision of the Primary Examiner dated November 21, 2008 finally rejecting claims 20-31 and 33-45, which are reproduced as the Claims Appendix of this Brief.

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The Commissioner is hereby authorized to charge any appropriate fees under 37 C.F.R. §§1.16, 1.17, and 1.21 that may be required by this paper, and to credit any overpayment, to Deposit Account No. 02-4800.

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I. Real Party in Interest

The present application is assigned to Rhodia Chimie. Rhodia Chimie is the real party in interest, and is the assignee of Application No. 10/589,209.

II. Related Appeals and Interferences

The Appellants' legal representative, or assignee, does not know of any other appeal or interferences which will affect or be directly affected by or have bearing on the Board's decision in the pending appeal.

III. Status of Claims

Claims 20-31 and 33-45 are pending, stand rejected, and are appealed.

IV. Status of Amendments

All amendments in this application have been entered. There have been no amendments filed subsequent to the Final Rejection of November 21, 2008. A Request for Reconsideration was filed on April 16, 2009.

V. Summary Claimed Subject Matter

Pursuant to 37 C.F.R. §41.37(1)(c)(v), the subject matter of each independent claim on appeal (claim 20) is cross-referenced to the specification and/or drawing Figures in the following table:

| Claim 20 | Cross-Reference to the Disclosure |
|---|---|
| 20. A composition consisting essentially of zirconium oxide and at least one additive | Page 1, lines 6-8; page 3, lines 5-13; page 4, line 35-page 5, line 5; page 15, lines 25-28; page 17, lines 12-15; page 19, lines 2-5, lines 15-18 and lines 27-30; and page 22, lines 3-8. |

| | |
|---|--|
| selected from oxides of praseodymium, lanthanum and neodymium, | Page 1, lines 6-8 and line 33-34; page 3, lines 5-13; page 15, lines 25-28; page 17, lines 12-15; page 19, lines 2-5, lines 15-18 and lines 27-30. |
| the composition having a specific surface area of at least 29 m ² /g after calcination for 10 hours at 1000°C. | Page 1, lines 35-36; page 4, lines 5-9; page 17, Table 1; page 18, Table 2; and page 20, Table 3 |

The portions of the specification have been identified above in order to comply with the requirements of 37 C.F.R. §41.37(c)(1)(v). The above references to the specification should not be construed as limiting the scope of the claimed subject matter to the various embodiments described in the specification, or otherwise as a vehicle for importing limitations into the claims from the specification.

VI. Grounds of Rejection to be Reviewed on Appeal

Whether Claims 20-30, 39-41 and 44-45 are unpatentable as being anticipated under 35 U.S.C. §102(b) or, in the alternative, as being obvious under 35 U.S.C. §103(a), over U.S. Patent No. 6,171,572 to Aozasa (hereafter "Aozasa").

Whether claims 31, 36-38 and 42 are unpatentable as being obvious under 35 U.S.C. §103(a) over Aozasa.

Whether claims 33-35 are unpatentable as being obvious under 35 U.S.C. §103(a) over Aozasa in view of U.S. Patent Application Publication No. 2003/0224931 to Yamamoto et al. (hereafter "Yamamoto et al.").

Whether claim 43 is unpatentable as being obvious under 35 U.S.C. §103(a) over Aozasa in view of U.S. Patent No. 5,063,192 to Murakami et al. (hereafter "Murakami et al.").

VII. Argument

A. Legal Principles

The Examiner bears the initial burden of factually supporting any *prima facie* conclusion of obviousness. See, e.g., M.P.E.P. §2142. All elements or limitations of a claim must be considered in evaluating the obviousness of that claim relative to the prior art. See, e.g., M.P.E.P. §2143.03. This legal conclusion must be reached on the basis of the facts gleaned from the prior art. See, e.g., M.P.E.P. §2142.

If an independent claim is nonobvious under 35 U.S.C. §103, then any claim depending therefrom is also nonobvious. *In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988).

The transitional phrase "consisting essentially of" limits the scope of a claim to the specified constituents, as well as those that did not materially affect the basic and novel characteristics of the claimed invention. *In re Hertz*, 537 F.2d 549, 551-552, 190 U.S.P.Q. 461, 463 (CCPA 1976). This phrase is understood to permit additional constituents, only if they do not "materially affect the basic and novel properties of the invention." *AK Steel Corp. v. Sollac*, 344 F.3d 1234, 68 U.S.P.Q.2d 1280, 1283 (Fed. Cir. 2003). This transitional phrase has also been characterized as excluding additional constituents that materially affect functionality of the claimed invention. *Kim v. ConAgra Foods Inc.*, 465 F.3d 1312, 80 U.S.P.Q.2d 1495, 1499 (Fed. Cir. 2006). Analyzing the meaning of the phrase "consisting essentially of" is an exercise in claim construction, as such, it is appropriate to examine, *inter alia*, the contents of the specification. *AK Steel Corp. v. Sollac*, 68 U.S.P.Q.2d at 1283.

When assertions are made based upon features that are not expressly disclosed in the prior art, the Federal Circuit has repeatedly stated that in order to establish the inherency of the missing element it must be shown that the missing element must necessarily be present in the reference, and would be recognized as such by those persons of ordinary skill in the art. *Continental Can Co. USA v. Monsanto Co.*, 948 F.2d 1264, 20 USPQ2d 1746, 1749-50 (Fed. Cir. 1991); *In re Oelrich*, 666 F.2d 578, 581, 212 USPQ 323, 326 (C.C.P.A. 1981) ("inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient");

Standard Oil Co. v. Montedison, S.p.A., 664 F.2d 356, 372, 212 USPQ 327, 341 (3rd Cir. 1981) (for a claim to be inherent in the prior art it "is not sufficient that a person following the disclosure sometimes obtain the result set forth in the [claim]; it must invariably happen").

If rejecting a claim requires reliance upon the alleged inherent features of the prior art, the Examiner must provide a basis in fact and/or technical reasoning to reasonably support the determination that the allegedly inherent characteristic necessarily flows from the teachings of the applied prior art. *Ex parte Levy*, 17 USPQ2d 1461, 1464 (Bd. Pat. App. & Inter. 1990) (emphasis in original) (Applicant's invention was directed to a biaxially oriented, flexible dilation catheter balloon (a tube which expands upon inflation) used, for example, in clearing the blood vessels of heart patients. The Examiner applied a U.S. patent to Schjeldahl which disclosed injection molding a tubular preform and then injecting air into the preform to expand it against a mold (blow molding). The reference did not directly state that the end product balloon was biaxially oriented. It did disclose that the balloon was "formed from a thin flexible inelastic, high tensile strength, biaxially oriented synthetic plastic material." Id. at 1462 (emphasis in original). The Examiner argued that Schjeldahl's balloon was inherently biaxially oriented. The Board reversed on the basis that the Examiner did not provide objective evidence or cogent technical reasoning to support the conclusion of inherency.)

B. Rejection of claims 20-30, 39-41 and 44-45 under 35 U.S.C. §102(b) as being anticipated by or, in the alternative, under 35 U.S.C. §103(a) as obvious over U.S. Patent No. 6,171,572 to Aozasa

1. Rejection of claim 20

The present invention is directed to compositions formulated such that they possess certain beneficial properties. One application for compositions formulated according to the principles of the present invention is as a catalyst. In particular, compositions formed according to the present invention may be useful as certain catalysts that are used for treating exhaust gases of internal combustion engines which are capable of not only oxidizing carbon monoxide and hydrocarbons present in exhaust gases, but are also capable of reducing nitrogen oxides also present in

these gases. Such catalysts are often referred to as "three-way" catalyst. These catalysts can be formed based on cerium oxide or zirconium oxide constituents (see, e.g., page 1, line 18-20 of the present specification), or can be formed based on a mixed cerium-zirconium oxides (see, e.g., Akkarat Wongkaew, "Effect of Cerium Oxide and Zirconium Oxide to Activity of Catalysts," *Chiang Mai J. Sci.* 2008; 35(1): 156-162; (hereafter "Wongkaew"); copy attached hereto in Evidence Appendix).

The present invention is directed to a composition based on zirconium oxide with specific additives, and not based on cerium oxide or a mixed cerium-zirconium oxide.

As well known to those familiar with the art, the presence of cerium oxide in such compositions provides extra oxygen from the lattice thereof and increases activity of the catalyst at relatively low temperatures. See, e.g., Wongkaew, page 157, section 1. However, the presence of cerium oxide in such compositions also renders the surface area of the catalyst less stable at higher temperatures.

The composition of the presently claimed invention seeks to provide a composition which possesses both sufficient catalytic activity, but also possesses a high degree of surface area stability at higher temperatures. As such, compositions formed according to the principles of the present invention purposely omit cerium oxide.

For example, as discussed on page 1 of the present specification, catalysts compositions containing cerium oxide are discussed as being conventional compositions (see, e.g. page 1, lines 18-20). Compositions formed according to the present invention are distinguished therefrom as being "based on zirconium oxide" (see, e.g., page 1, line 32) in order to provide increased surface area stability at high temperatures (see, e.g. page 1, lines 24-26).

Moreover, six specific examples of compositions formulated according to the present invention are disclosed in the present specification (Examples 1-6), all of which omit cerium oxide. A Comparative Example is also disclosed (Example 7) which includes cerium oxide. As the Board knows, comparative examples are examples which do not correspond to the present invention, but instead highlight differences therefrom.

A composition formed according to the principles of the present invention as set forth in claim 20. Claim 20 recites:

20. A composition consisting essentially of zirconium oxide and at least one additive selected from oxides of praseodymium, lanthanum and neodymium, the composition having a specific surface area of at least 29 m²/g after calcination for 10 hours at 1000°C.

Aozasa is directed to a zirconium-cerium mixed oxide, which may optionally comprise one or more additives. However, Aozasa clearly fails to anticipate, or render obvious, the composition as set forth in claim 20.

As evident from the above, claim 20 is directed to a composition "consisting essentially of zirconium oxide and at least one additive selected from oxides of praseodymium, lanthanum and neodymium." By contrast, Aozasa teaches compositions limited to a composite mixed oxide composed of both zirconium and cerium in substantial amounts.

The presence of cerium clearly has a material impact on the characteristics of such compounds.

Evidence of this material effect can be found in the discussion above of the contents of Wongkaew, and can also be found in the disclosure of Aozasa itself:

... cerium oxide-containing materials, which have oxygen absorbing and desorbing capability originated in cerium oxide, i.e., the properties of absorbing oxygen under the oxidizing atmosphere and desorbing oxygen under the reducing atmosphere. With this oxygen absorbing and desorbing capability, the cerium oxide-containing materials purify noxious components in exhaust gases such as hydrocarbons, carbon monoxide, and nitrogen oxides at excellent efficiency. (column 1, lines 20-28)

Thus, the evidence is irrefutable that the presence of cerium oxide materially alters the fundamental catalytic properties of such compositions.

Although it is stated in MPEP 2111.03 that in certain situations "consisting essentially of" can be construed as equivalent to "comprising," such an interpretation is inappropriate where it is shown that the introduction of additional components

would materially change the characteristics of the invention. For at least the reasons discussed above, there is irrefutable evidence that the presence of cerium oxide has a material affect on the catalytic activity and surface area stability of compositions such as those embodied by the presently claimed invention. Thus, transitional phrase "consisting essentially of" appearing in the claims of the present application should not be construed so as to include or encompass compositions such as those described by Aozasa, which are in the form of a mixed or composite oxide of both zirconium and cerium. Therefore, the rejection is improper and must be reversed.

In addition, as a matter of claim interpretation, it is abundantly clear from the present specification, for at least the reasons discussed above, that compositions formed according to the principles of the present invention are formulated such that they purposely exclude cerium oxide.

In addition, Aozasa teaches that if the cerium oxide content of the composite zirconium/cerium oxide is less than 5% by wt. (i.e., zirconium content more than 95), then "the oxygen absorbing and desorbing capability originating from cerium oxide is insufficiently exhibited" (column 4, lines 26-28). Thus, Aozasa teaches away from elimination of cerium oxide from the composition described therein.

As acknowledged on page 3 of the Official Action, Aozasa also does not teach the claimed specific surface area after ten hours of calcination at 1000°C. Nevertheless, it is asserted that the composition as taught by Aozasa would inherently possess the properties cited by the presently claimed invention. This assertion is respectfully traversed.

As discussed above, the presence of cerium in compounds of the type set forth in the claims of the present application has a material effect on the catalytic activity and surface area stability of such compositions. Thus, the premise that the compositions that both contain and lack cerium must necessarily possess the same properties, is clearly unfounded. Therefore, the rejection is improper and must be reversed for at least these additional reasons.

2. Rejection of claims 21-30, 39-41 and 44-45

The rejection of claims 21-30, 39-41 and 44-45 standard fall together with the rejection of claim 20.

C. Rejection of claims 31, 36-38 and 42 as being obvious under 35 U.S.C. §103(a) over Aozasa

It is alleged on pages 6-7 of the Final Rejection that the additional features cited in the above-listed claims are also either inherent, or would be obvious, in view of Aozasa. For at least the same reasons noted above, Aozasa fails to disclose, or even suggest, a composition consisting essentially of zirconium oxide and at least one additive, as required by the presently claimed invention. Thus, the above-listed claims are also distinguishable over Aozasa for at least the same reasons noted above. The rejection is improper and must be reversed.

D. Rejection of claims 33-35 as being obvious under 35 U.S.C. §103(a) over Aozasa in view of Yamamoto et al.

1. Rejection of claim 33

Claim 33 is directed to a method for preparing the composition of claim 20. Thus, the result of the recited method is the production of a composition which consists essentially of zirconium oxide and at least one additive selected from oxides of praseodymium, lanthanum and neodymium.

For at least the reasons explained above, Aozasa fails to disclose any method whatsoever which would result in the production of such a composition.

Yamamoto et al. is cited as allegedly teaching a method of making a zirconium-cerium oxide catalyst material optionally comprising alumina, silica or titania which includes formation of an aqueous mixture of cerium nitrate and zirconium oxynitrate, adding hydrogen peroxide and ammonia, forming a precipitate, adding cationic and anionic surfactants, and calcining the resultant mixture. It is further alleged that *Yamamoto et al.* teaches decomposition of zirconium and cerium compounds upon heating, and the addition of a surfactant to form homogenous precursor, followed by calcination. It is also asserted on page 7 of the Official Action,

that Yamamoto et al. teaches the use of a suitable surfactant to improve the diffusion properties of the additive particles. However, even if the alleged teachings of Yamamoto et al. were applied in the manner suggested, the claimed invention would not result. Namely, the alleged teachings of Yamamoto et al. fail to cure the deficiencies previously noted above in connection with the primary reference to Aozasa. Therefore, for at least this reason, the rejection should be withdrawn.

Moreover, claim 33 requires a method which includes "forming a mixture comprising compounds consisting essentially of compounds of zirconium and the at least one additive." By contrast, neither Aozasa, nor Yamamoto et al., either taken alone or in combination, disclose or suggest a method which includes the step of forming such a mixture. Thus, for at least this additional reason, reconsideration and withdrawal of the rejection is respectfully requested.

2. Rejection of claims 34-35

The rejection of claims 34-35 standard fall together with the rejection of claim 33.

E. Rejection of Claim 43 as being obvious under 35 U.S.C. §103(a) over Aozasa in view of Murakami et al.

It is alleged on page 8 of the Final Rejection that it would have been obvious to one of ordinary skill in the art, in light of the teachings of Murakami et al., to have applied the composition taught by Aozasa to a substrate such as a honeycomb structure. Applicants do not concede to the correctness of these assertions. Nevertheless, the applied teachings of Murakami et al. are insufficient to cure the deficiencies previously noted above in connection with the teachings of Aozasa. Namely, even if the teachings of Murakami et al. were applied to Aozasa exactly in the manner proposed in the grounds for rejection, the claimed invention would not result. Thus, the rejection is improper and must be reversed.

VIII. Claims Appendix

See attached Claims Appendix for a copy of the claims involved in the appeal.

IX. Evidence Appendix

See attached Evidence Appendix for copies of evidence relied upon by Appellant.

X. Related Proceedings Appendix

See attached Related Proceedings Appendix for copies of decisions identified in Section II, supra.

Respectfully submitted,

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Date August 18, 2009

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VIII. CLAIMS APPENDIX

The Appealed Claims

1. - 19. (Canceled)

20. A composition consisting essentially of zirconium oxide and at least one additive selected from oxides of praseodymium, lanthanum and neodymium, the composition having a specific surface area of at least 29 m²/g after calcination for 10 hours at 1000°C.

21. The composition as claimed in claim 20, wherein the specific surface area is at least 35 m²/g after calcination for 10 hours at 1000°C.

22. The composition as claimed in claim 21, wherein the specific surface area is at least 50 m m²/g after calcination for 10 hours at 1000°C.

23. The composition as claimed in claim 20, having a specific surface area of at least 10 m²/g after calcination for 4 hours at 1100°C.

24. The composition as claimed in claim 23, wherein the specific surface area is at least 15 m²/g after calcination for 4 hours at 1100°C.

25. The composition as claimed in claim 21, having a specific surface area of at least 2 m²/g after calcination for 10 hours at 1200°C.

26. The composition as claimed in claim 20, having a specific surface area of at least 45 m²/g after calcination for 4 hours at 900°C.

27. The composition as claimed in claim 26, wherein the specific surface area is at least 50 m²/g after calcination for 4 hours at 900°C.

28. The composition as claimed in claim 20, having an additive content which does not exceed 50% by weight of additive oxide with respect to the weight of the composition.

29. The composition as claimed in claim 28, wherein the additive content is 10% to 40%.

30. The composition as claimed in claim 29, wherein the additive content is 10% to 30%.

31. The composition as claimed in claim 20, further having mesopores 10 nm to 500 nm in size.

32. (Canceled)

33. A method for preparing the composition of claim 20, the method comprising:

- (a) forming a mixture comprising compounds consisting essentially of compounds of zirconium and the at least one additive;
- (b) contacting the mixture of (a) with a basic compound whereby a precipitate is obtained;
- (c) heating the precipitate of (b) in a liquid medium;
- (d) adding a compound to the precipitate of (c), said compound being an anionic surfactant, nonionic surfactant, polyethyleneglycol, carboxylic acid, a salt thereof, or a carboxymethylated fatty alcohol ethoxylate; and
- (e) calcining the precipitate of (d).

34. The method as claimed in claim 33, wherein the compounds of zirconium, and of additive are nitrates, acetates or chlorides.

35. The method as claimed in claim 33, wherein the heating of the precipitate is carried out at a temperature of at least 100°C.

36. A catalytic system, comprising the composition of claim 20.
37. The catalytic system as claimed in claim 36, further comprising a transition metal or a precious metal, supported by the composition.
38. A method for treating exhaust gases of internal combustion engines, comprising treating said gases in the presence of the catalyst system as defined in claim 37.
39. The composition as claimed in claim 21, wherein the specific surface area is at least 40 m²/g after calcination for 10 hours at 1000°C.
40. The composition as claimed in claim 25, wherein the specific surface area is at least 3 m²/g after calcination for 10 hours at 1200°C.
41. The composition as claimed in claim 27, wherein the specific surface area is at least 55 m²/g after calcination for 4 hours at 900°C.
42. A catalyst support comprising the composition of claim 20.
43. A substrate having a wash coat applied thereon, the wash coat comprising the composition of claim 20.
44. The composition as claimed in claim 20, wherein the zirconium oxide and the at least one additive form a solid solution.
45. The composition as claimed in claim 20, wherein the composition is in the form of a mixture of different phases.

IX. EVIDENCE APPENDIX

Akkarat Wongkaew, "Effect of Cerium Oxide and Zirconium Oxide to Activity of Catalysts, *Chiang Mai J. Sci.* 2008; 35(1), pp. 156-162.



Effect of Cerium Oxide and Zirconium Oxide to Activity of Catalysts

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ABSTRACT

In this work, the activities of platinum over alumina promoted with cerium oxide and zirconium oxide were investigated. Each support contained various weight percents of cerium oxide and zirconium oxide to alumina was prepared by sol gel method. The weight percent of cerium oxide to zirconium oxide was kept constant at 60 to 40. Specific surface areas of each support were measured. It was found that the addition of 20% CeO_2 - ZrO_2 in alumina support offered the highest specific surface area of 215 m²/g. Furthermore, crystalline phase and size of mixed oxide were determined by XRD. XRD results also showed that $\text{Ce}_2\text{Zr}_2\text{O}_7$ was formed in the support. The amount of cerium oxide, zirconium oxide and alumina had a strong effect to their crystalline size in the final form. Then, each support was impregnated with 1%Pt loading and tested its activity to CO oxidation reaction. The results showed that $T_{1/2}$ of each catalyst was 210°C, 139°C, 145°C, 150°C and 261°C for a 1%Pt/ Al_2O_3 , a 1%Pt/20% CeO_2 - ZrO_2 / Al_2O_3 , a 1%Pt/40% CeO_2 - ZrO_2 / Al_2O_3 , a 1%Pt/60% CeO_2 - ZrO_2 / Al_2O_3 and a 1%Pt/ CeO_2 - ZrO_2 , respectively. The enhancement of activity of platinum over alumina catalyst resulted from an oxygen storage property of cerium oxide together with zirconium oxide. Finally, the 1%Pt/40% CeO_2 - ZrO_2 / Al_2O_3 has showed the best activity to CO oxidation.

Keywords: CO oxidation, promoter, cerium oxide, zirconium oxide, oxygen storage.

1. INTRODUCTION

CO oxidation is the reaction used for removing or eliminating CO by burning it with oxygen or air. In general, this reaction rarely occurs unless there is some suitable catalyst present. Several metals together with supports such as Au/ Al_2O_3 , Au/ CeO_2 , Pd/ Al_2O_3 , Rh/ Al_2O_3 , Pt/ Al_2O_3 or Pt over zeolite have been widely investigated for this reaction. However, platinum over alumina seems to be the well known catalyst extensively studied the activity and the mechanism to CO oxidation over four

decades. This is due to the stability and activity of platinum [1]. Unfortunately, this catalyst is active to this reaction at temperatures greater than 160°C. This causes by the chemisorptions of CO over platinum active sites at low temperatures and the competition between CO molecules and oxygen molecules to adsorb on platinum. To develop this catalyst to be active at lower range of temperatures, it could be done by either adding other compounds such as cerium oxide, iron oxide

and so on [2,3] or using suitable preparation method [4]. As known from many works on three way catalysts, cerium oxide is used in order to provide extra oxygen from their lattice in the condition of deficiency of oxygen [5-7]. This is so called an oxygen storage property. Moreover, zirconium oxide is well known as temperature resistant compound. The use of it combining together with cerium oxide offers the better the oxygen storage property [8,9]. However, the suitable amount of cerium oxide and zirconium oxide in alumina support for the improvement of platinum catalyst is still unrevealed.

In this work, catalysts cooperated together with different amounts of cerium oxide, zirconium oxide and aluminium oxide prepared by sol gel method and impregnated with 1%Pt were investigated their activities to CO oxidation. From this study, the effect of addition of cerium oxide and zirconium oxide into the support, $\text{CeO}_2\text{-ZrO}_2\text{/Al}_2\text{O}_3$, was studied.

2. MATERIALS AND METHODS

2.1 Catalyst preparation

Aluminium isopropoxide, cerium (III) nitrate and zirconium nitrate obtained from Sigma-Aldrich Company were used in this preparation. Mixed oxide of ceria, zirconia and alumina was prepared by sol gel method. Aluminium isopropoxide was weighted and then added into hot deionized water. The solution was kept stirring to obtain uniformity. Next, nitric acid was added into the solution until this solution became clear. After stirring 30 min., cerium (III) nitrate and zirconium nitrate were added into the obtained solution, respectively. The solution was aged overnight and is called "sol". Next, the sol was heated to obtain gel. The gel was aged overnight. After aging, the gel was dried at 110°C for 10 hr. followed by calcined at 500°C for 8 hr. The final oxide was ground and sieved to 100

mesh. All supports containing mixed oxide were impregnated with 1% platinum loading by incipient wetness impregnation.

For catalyst characterization, specific surface areas of each support were measured by Autosorption-1 (Quantachrome Corporation). Phase and crystalline size of each mixed oxide was analyzed by X-ray diffractometer from Bruker AXS Model D8 Discover.

2.2 Activity test

All supports and catalysts were tested their activities to CO oxidation in the micro-reactor. Reaction temperature was controlled by temperature controller with K-type thermocouple placed on the top of the catalyst bed. The range of reaction temperatures was 100-300°C. The amount of catalysts used was 80 mg. Gas composition contained 1%CO, 1%O₂ and 98%He. The total gas flow rate was adjusted to achieve 100 cc/min. The mixed gas was delivered by a mass flow controller (Porter Company). The accuracy of flow was within 1%. A Varian CP 3800 gas chromatograph (GC) equipped with carbosphere 80/100 and a thermal conductivity detector was used to determine the inlet and outlet gas compositions. Before, each catalyst was tested its activity to CO oxidation, it was purged under H₂ gas at 400°C for 4hr.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

In this work, supports contained various amount of cerium oxide, zirconium oxide and aluminium oxide was prepared by sol gel method. The weight percent between cerium oxide and zirconium oxide was kept constant at 60 to 40. The weight percents between both mentioned oxides and aluminium oxide were varied to the ratio of 100 to 0, 60 to 40, 40 to 60, 20 to 80 and 0 to 100. For example, the first sample contained only cerium oxide

and zirconium oxide with the weight percent of 60 to 40. The second sample contained 60% of cerium oxide and zirconium oxide and 40% of aluminium oxide. This means the second sample containing 36% cerium oxide and 24% zirconium oxide (weight ratio of 60 to 40). The last sample contained only aluminium oxide. Then, all supports were

measured their specific surface areas by Autosorption-1(Quantachrom). The results from this study could be used to explain the effect of the addition of cerium oxide and zirconium oxide to the physical properties of the final supports. The results were showed in Table 1.

Table 1. Specific surface area of supports with different amount of cerium oxide and zirconium oxide to aluminium oxide (weight ratio of cerium oxide and zirconium oxide was kept constant at 60:40).

| Sample No. | Supports | Specific surface area, m^2/g |
|------------|---|--|
| 1 | Al_2O_3 (Aldrich company) | 155 |
| 2 | Al_2O_3 (sol gel) | 190 |
| 3 | 20%wt CeO_2 - ZrO_2 / Al_2O_3 | 215 |
| 4 | 40%wt CeO_2 - ZrO_2 / Al_2O_3 | 194 |
| 5 | 60%wt CeO_2 - ZrO_2 / Al_2O_3 | 147 |
| 6 | 100%wt CeO_2 - ZrO_2 | 47 |

As can be seen from Table 1, sample 1 was pure alumina obtained from Aldrich company. Its specific area was $155 \text{ m}^2/\text{g}$ while specific surface area of sample 2, pure alumina prepared by sol gel method, was $190 \text{ m}^2/\text{g}$. From this result, it seemed that sol gel method offers high specific surface areas for the final oxides. This causes from solvent trapped inside the solid structure (gel). When gel is dry, solvent evaporates from the solid network and in turn leave empty pores inside the solid. Therefore, the final oxide prepared by this method has high specific surface area. Sample 3 was a mixed oxide of cerium oxide, zirconium oxide and alumina. Interestingly, the specific surface area of sample 3 was 13% greater than that of sample 2. This result was in agreement with works done by Matina T. et.al. [10]. They prepared different ratio of

mixed oxides of cerium oxide and zirconium oxide. They found that an increase in weight percent of zirconium oxide increased specific surface area of the final oxides. This result implied that the presence of cerium oxide and zirconium oxide improved thermal resistance for the final oxide. However, further increasing amount of cerium oxide and zirconium oxide led to decreasing of specific surface area as observed from samples no. 4-6. This may cause from the growth of crystalline size of cerium oxide and zirconium oxide. From these results, it can be concluded that amount of cerium oxide and zirconium oxide in the mixed oxides has strong effect to the specific surface area of the final oxides. Indeed, the 20% doping mixed oxides of cerium and zirconium offered the highest specific surface area.

Furthermore, these supports were analyzed phase and crystalline size by X-ray

diffraction. The results were shown in Figure 1.

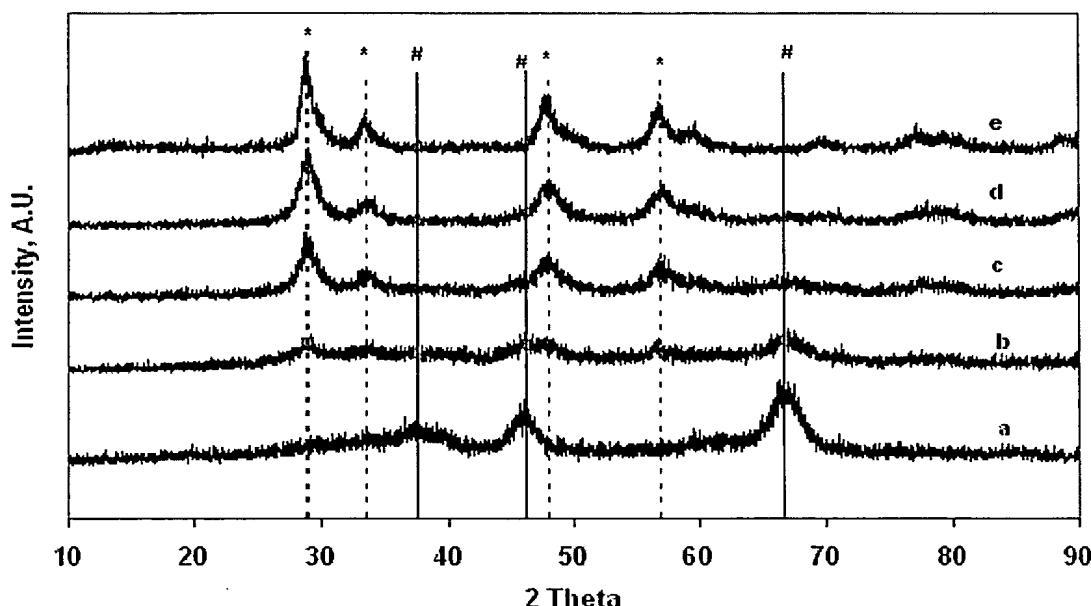


Figure 1. XRD patterns of each support: (a) pure alumina, (b) 20% CeO_2 - ZrO_2 / Al_2O_3 , (c) 40% CeO_2 - ZrO_2 / Al_2O_3 , (d) 60% CeO_2 - ZrO_2 / Al_2O_3 and (e) 100% CeO_2 - ZrO_2 ; *refers to reference peaks of $\text{Ce}_2\text{Zr}_2\text{O}_7$ and # refers to reference peaks of Al_2O_3 .

As can be seen in Figure 1, no XRD patterns of CeO_2 and ZrO_2 were observed. XRD patterns of supports matched with XRD patterns of $\text{Ce}_2\text{Zr}_2\text{O}_7$ and Al_2O_3 . This may be explained as following: During condensation reaction in sol gel process, hydroxyl groups from hydrolysis reaction can combine together and form Ce-O-Zr bonds. Therefore, vertical dash lines in the samples at 2 theta of 29°, 33.5°, 48° and 57° were observed. These angles are corresponding to reference peaks for $\text{Ce}_2\text{Zr}_2\text{O}_7$. In Figure 1 a, a sample contained pure alumina only. The XRD pattern of this sample was in agreement with the reference peak pattern of pure alumina. The addition of 20% cerium oxide and zirconium oxide (Figure 1 b) reduced the intensity of

aluminium oxide patterns and in turn observed the other peaks in the same positions as a reference pattern of $\text{Ce}_2\text{Zr}_2\text{O}_7$. As amount of cerium oxide and zirconium oxide inside samples increased, the intensities of XRD patterns at these positions increased as shown in Figure 1 c, d and e. This meant crystalline size of $\text{Ce}_2\text{Zr}_2\text{O}_7$ was getting larger. The growth of metal crystalline size may cause the reduction of the specific surface area of mixed oxides.

3.2 Activity of pure supports

Pure supports were tested their activities to CO oxidation before they were impregnated with 1%Pt. The results were shown in Figure 2.

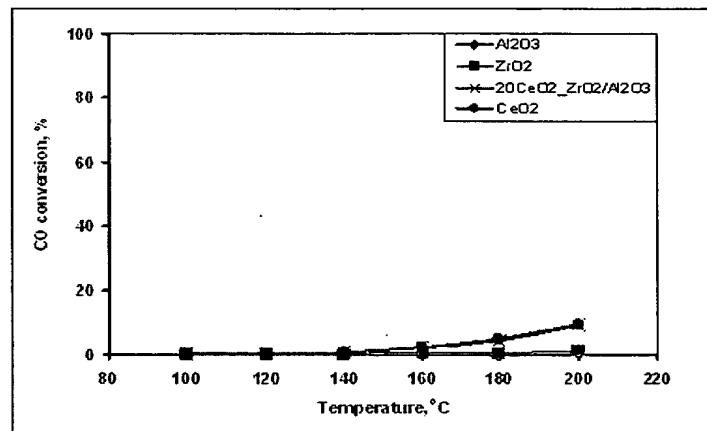


Figure 2. Activities of pure supports to CO oxidation. Gas composition: 1%CO, 1%O₂ and He as balance. SV=75,000cc/g/h.

In Figure 2, x-axis represents reaction temperature (°C), and y-axis represents CO conversion (%). The studied temperatures were in the range of 100°C to 200°C. As reaction temperatures increased from 100°C to 140 °C, CO conversions were nearly zero for all pure supports. When reaction temperatures were greater than 150°C, CO conversion slightly increased for 2 supports: 20%CeO₂-ZrO₂/Al₂O₃ and CeO₂. However, CO conversion was less than 10% even at reaction temperature of 200 °C. These results

implied that pure supports were not active to the reaction.

3.3 Effect of amount of cerium oxide and cerium oxide in support

Each support with various weight percent of cerium oxide, zirconium oxide and alumina was impregnated with 1%Pt loading. Then, they were tested their activities to CO oxidation reaction. The results were showed in Figure 3.

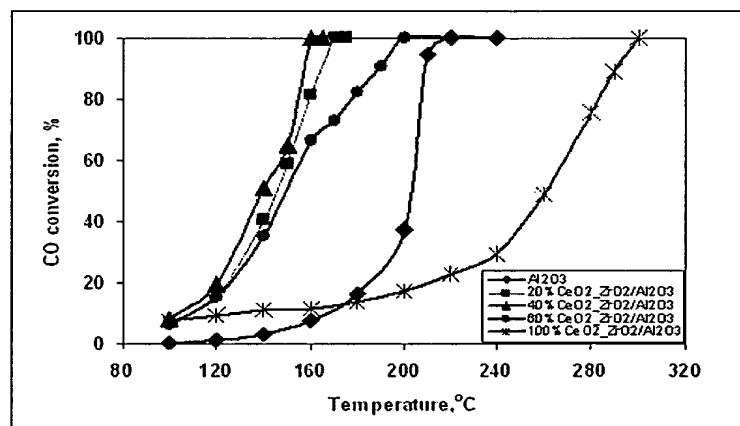


Figure 3. Activities of catalysts to CO oxidation reaction. Each catalyst contained various amounts of cerium oxide and zirconium oxide and aluminium oxide loading with 1%Pt. Gas composition: 1%CO, 1%O₂ and He as balance. SV=75,000cc/g/h.

In Figure 3, CO conversion increased with increasing of reaction temperatures for all catalysts. However, the activities of these catalysts were different. For a 1%Pt/Al₂O₃, CO conversion slowly increased with an increase of reaction temperatures until reaction temperatures were greater than 160°C. Above this temperature, CO conversions dramatically increased and reached 100% at 220°C. This could be explained in terms of T_{1/2} defined as temperature at which half of CO concentration was consumed by the reaction. T_{1/2} of this catalyst was approximately 201°C. The addition of 20% CeO₂-ZrO₂ into aluminium oxide support incredibly enhanced the activity of platinum based catalysts. The active temperatures lowered down by 56°C and T_{1/2} of this catalyst was 145°C. This may cause by the presence of CeO₂ together with ZrO₂. This result was confirmed by the work done by Mattos, L.V., and Noronha, F.B.[11]. They studied the oxygen transfer capacity and oxygen storage property of CeO₂-ZrO₂ used as a support for platinum in partial oxidation reaction of ethanol. They found that in the absence of cerium oxide, the catalyst can store oxygen about 9 mmol/g of catalyst while the catalyst contained CeO₂ without zirconium oxide could store oxygen about 194mmol/g of catalyst and the catalyst combining both cerium and zirconium oxides with the molar ratio of 50 to 50 (Pt/Ce_{0.50}Zr_{0.50}O₂) could store oxygen up to 696mmol/g of catalyst. Therefore, the presence of cerium oxide and zirconium oxide in the platinum over alumina catalysts improved the activity of the catalyst to CO oxidation. Lattice oxygen from cerium oxide could transfer and react with CO adsorbed over Pt active sites at the interface between Pt and cerium oxide [12]. Further investigation was conducted on varying the weight percent of cerium and zirconium oxides in aluminium oxide support.

As can be seen from Figure 3, a 1%Pt/40%CeO₂-ZrO₂/Al₂O₃ performed the best activity to CO oxidation. T_{1/2} of this catalyst was 139°C while T_{1/2} of others were 145°C, 150°C and 261°C for a 1%Pt/20% CeO₂-ZrO₂/Al₂O₃, a 1%Pt/60%CeO₂-ZrO₂/Al₂O₃, and a 1%Pt/CeO₂-ZrO₂, respectively. The differences in T_{1/2} for each catalyst may cause from the specific surface area and crystalline size of cerium zirconium oxide. As known from Table 1, an increase of the amount of cerium oxide and zirconium oxide led to decreasing of specific surface area of the sample and in turn increasing the peak intensity from XRD pattern. This meant a growth of crystalline size of mixed oxide. These results may cause the difference in Pt dispersion of each catalyst. As been known that the activity of Pt based catalyst to CO oxidation depends on crystalline size of Pt. The highly dispersion Pt or small crystalline size Pt led to the better the activity to CO oxidation [13]. According to the specific surface area results, they implied that an increase in weight percent of cerium oxide and zirconium oxide in alumina lowered the degree of dispersion of Pt in the sample. Therefore, the last sample, no alumina in the support, was the worst activity to CO oxidation. However, for 20%CeO₂-ZrO₂/Al₂O₃ and 40%CeO₂-ZrO₂/Al₂O₃, both has similar specific surface area. Their activities to CO oxidation were close within error. In this case, the oxygen storage properties caused from the presence of cerium oxide and zirconium oxide was a dominant evidence to enhance the reaction.

4. CONCLUSION

The activity to CO oxidation of platinum over alumina catalysts can be improved by adding some compounds into the alumina support. In this work, the results showed that the addition of 40%CeO₂-ZrO₂ into alumina

support followed by platinum to obtain a 1%Pt/40%CeO₂-ZrO₂/Al₂O₃ dramatically enhanced the activity of Pt based catalyst to CO oxidation and showed the best performance to CO oxidation. T_{1/2} of the 1%Pt/Al₂O₃ was 201°C and T_{1/2} of the 1%Pt/40%CeO₂/Al₂O₃ was 139°C. This was due to an oxygen storage capacity of cerium oxide together with zirconium oxide. However, further increasing the amount of cerium oxide and zirconium oxide into the alumina support lowered the activity of the catalyst to this reaction. This may cause from the lower of the specific surface area of the mixed oxide supports and thus in turn lead to less dispersion of Pt.

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X. RELATED PROCEEDINGS APPENDIX

None.